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Optimizing Organic Dye Degradation in a Low Power Atmospheric Pressure Plasma Discharge

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14. ABSTRACT

Plasma-based water treatment has emerged as one of the most effective advanced oxidation processes. One of the major issues inhibiting the development of plasma-based water treatment is attributed to large energy consumption. In order to optimize organic contaminant removal, the production of oxidizing radicals in the gas phase and their effective delivery to the water need to be maximized. This study demonstrates the degradation of an industrial dye, indigo carmine, dissolved in water using a nanosecond pulsed dielectric barrier discharge in a custom reactor. The degradation rate of the indigo carmine is dependent on various operating parameters, such as the applied voltage, gas flow, and gas mixture. The rate of degradation can be increased by applying higher voltages and introducing a small amount of air with helium.

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I.   Introduction

With global water pollution increasing, finding a dependable, cost-effective method to treat water has never been more vital. One of the major contributors towards water pollution is waste water discharged from textile plants. Additionally, the transfer of polluted ballast water between ecosystems has contributed to the spread of invasive species/microorganisms and harmful organic contaminants.[1] It is estimated that about 10^{20} bacteria and viruses in ballast water are annually transported into ports of the lower Chesapeake Bay.[2] In order to prevent further pollution, stricter regulations regarding water treatment are beginning to be implemented, which more effective methods of treatment will be needed. Traditional forms of ballast and textile waste water treatment includes the application of ultrasound and cavitation, UV irradiation, and the utilization of oxidants such as chlorine and ozone.[1, 3] These methods are often limited by high energy requirements or production of harmful chemical byproducts. In order to find a more efficient method to treat contaminated water, advanced oxidation processes (AOPs) have become an active field of research. These oxidation processes have the ability to mineralize organic contaminants into carbon dioxide and water without the creation of hazardous byproducts.[3] Treating water with atmospheric pressure plasma is an AOP that has gained a lot of attention due to its unique property of creating a large variety of highly reactive species such as, $OH^\bullet$, $O^\bullet$, $H^\bullet$, $HO_2^\bullet$, O_2^-, O_3, H_2O_2, and H_2.[4] These species, along with the simultaneous production of other free radicals, charged particles, UV radiation, and shockwaves provide a very effective way to degrade organic compounds.[5] Despite the many advantages, the implementation of plasma-based water treatment has been heavily constrained due to its large energy demands. In order to lower energy costs, operating parameters must be optimized to increase organic contaminant removal while minimizing power requirements. In this work, the degradation of an organic contaminant, indigo carmine, by a nanosecond pulsed dielectric barrier discharge was investigated. The effect of applied voltage, gas flows, and gas mixtures on the water chemistry was studied in order to provide a better understanding of the interactions between the dye and plasma.

II.   Experimental Setup

A. Reactor design and operation

The first reactor designs (not shown) utilized a non-circulating water supply and a small plasma discharge. The system was ineffective in treating any significant water volume in a timely manner. The reasons were assumed to be that with a stagnant water volume, the water surface-to-volume ratio is relatively small and so the requisite species were note being effectively delivered via the plasma-water interaction. The shortcomings of this design led to the development of a reactor which was designed to maximize the plasma volume, while also maximizing the water surface area to volume ratio. Accordingly, a system was built that simultaneously introduced both fluid and gas into the discharge volume, which generated a mist that flowed through the plasma volume, thereby increasing the water surface area to volume ratio resulting in a larger plasma-liquid interface. This proved to be a more efficient approach to treating a larger volume of water compared to the system where the water was stagnant.

The experimental setup is shown in Fig. 1. The discharge chamber consisted of a 3/8" (9.525 mm) ID x 1/2" (12.700 mm) OD glass tube aligned vertically with two electrodes consisting of two 10 mm wide copper strips wrapped tightly around the tube. Mass flow controllers introduced

helium or a helium and air mixture into the tube through a T-nozzle placed at the top of the tube. Flow rates of gas ranged from 2530-10000 cm³/min (SCCM). Because helium has a lower breakdown voltage compared to the surrounding atmospheric air, a discharge plasma formed between the electrodes on the inside of the tube. The dye solution, consisting of indigo carmine (HiMedia) in distilled water, was pumped from a reservoir via peristaltic pump at a flow rate of 100 ml/min and sprayed into the discharge tube through the T-nozzle. A 3-D printed polylactic acid (PLA) reducer was fit inside the T-nozzle in order reduce the water droplet volume. The simultaneous delivery of gas and liquid created a mist-like spray that increased the surface area of the liquid. After the mist came in contact with the tube, a thin water film was formed, which flowed down the tube and back into the reservoir. Pulsed high voltages were applied between the electrodes using a pulsed power supply (Eagle Harbor Technologies Nanosecond Pulser NSP-120-20-F) for a duration of 100 ns at a frequency of 5000 Hz. Voltages varied from 10 kV to 20 kV.
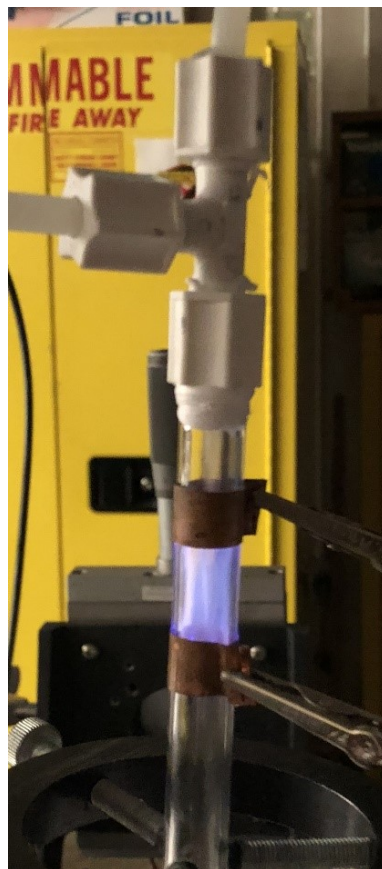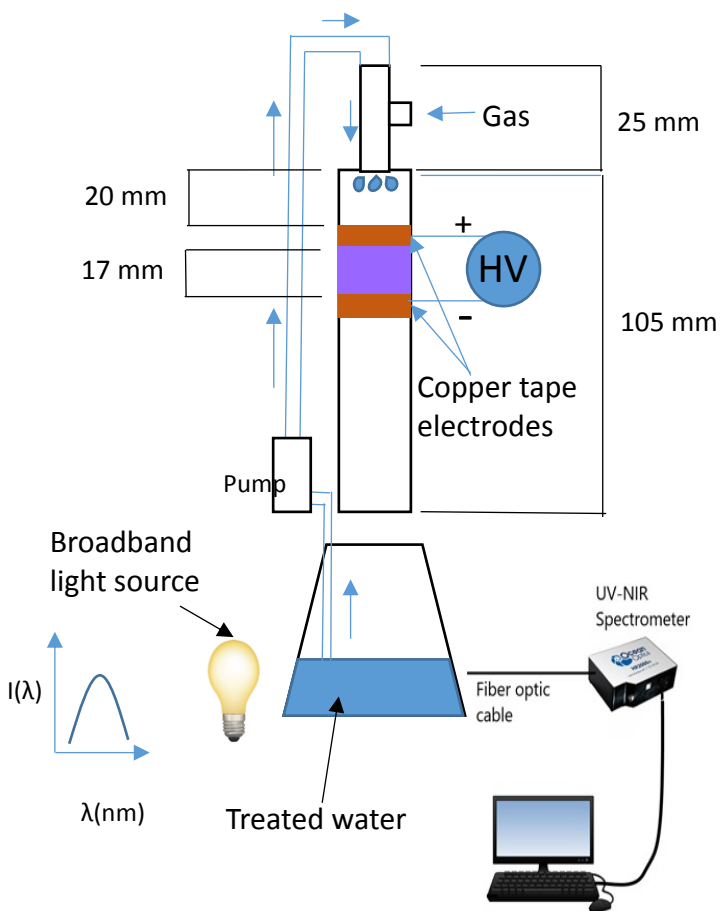

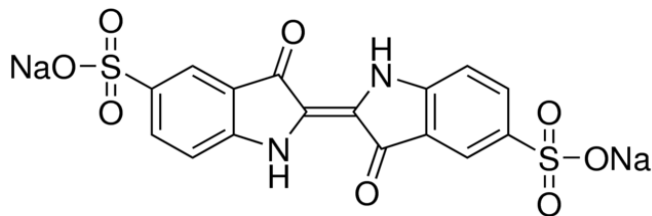**Fig. 1.** Diagram of experimental setup and image of reactor.

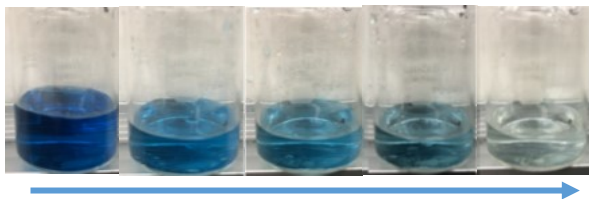**Fig. 2.** Molecular structure of indigo carmine.[7]

Fig. 3. Decolorization of indigo carmine solution with increasing treatment time. Images show the as-prepared solution (left) and the solution after one min intervals of plasma treatment.

B.   Indigo carmine degradation measurements

Indigo carmine ($C_{18}H_8N_2Na_2O_8S_2$), a textile dye and pH indicator (color transition range between 11.6 and 14.0), was used as an organic contaminant. Its molecular structure has a C=C bond in the center (Fig. 2), which is highly reactive and responsible for decolorization. For all measurements, a solution of dye and deionized water was used with a concentration 30 mg/L. To assess degradation, the solution in the reservoir was illuminated with a tungsten strip lamp (Optronics Laboratories OL-550) and the absorption spectrum of the indigo carmine solution was monitored using a UV-NIR spectrometer (Ocean Optics HR2000). For lower wavelengths, the solution was illuminated with a deuterium arc lamp (Oriel 63345) and the absorption was monitored with a UV spectrometer (Ocean Optics Maya 2000 Pro). Indigo carmine has three major absorption peaks at 240 nm, 286 nm, and 610 nm; the peak at 610 nm is responsible for its blue color, therefore this study measures the absorbance at 610 nm.[6] The pH of the solution was also monitored using a digital pH Meter (VantaKool). A typical treatment is shown in Fig. 3, where decolorization is seen to occur over the course of several minutes of plasma exposure time.

III.   Results and Discussion

A. Applied Voltage:

Figure 4 shows the effect of applied voltages from 12 to 18 kV on the absorbance during treatment of a 15 mL solution of indigo carmine. A constant helium flow rate of 4480 SCCM was used for all measurements. The absorption was measured and averaged over 596-620 nm using an integration time of 250 ms. Data values were normalized such that the initial absorbance is equivalent to 1. As shown in Fig. 4, the differences of the final absorbance after 350 sec of treatment between the varied voltages is not dramatic.

Figure 5 shows the decay rate constant of the absorbance as a function of time. The absorbance function was fitted by an exponential decay equation:

$$y(t) = A_1\, e^{-k/t} + y_o \tag{1}$$

where y is the absorbance, A_1 is a constant, k is the decay rate constant, t is treatment time, and y_o is an arbitrary fitting constant. The decay rate from 12 to 16 kV did not show much variation. However, at 18 kV there was a significant increase.
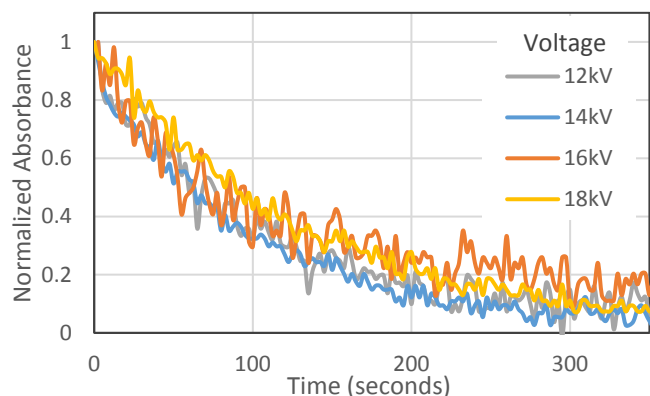
Fig. 4. Effect of applied voltage on absorbance (averaged from 596 to 620 nm) of 15 mL indigo carmine solution at 4480 SCCM.
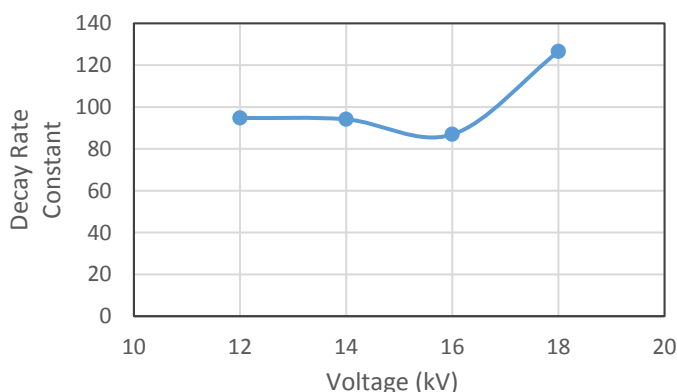

Fig. 5. Decay rate constant of applied voltages at 4480 SCCM and 350 sec treatment time.

In Fig. 6, the pH was measured for different treatment times in order to determine whether pH was correlated with decolorization. A dramatic drop from the initial pH of 5.9 to 4.2 at 30 seconds of treatment time was seen. After 30 seconds, there was a significant decrease in the rate of pH change, as the solutions' pH with an applied voltage of 14 kV and 16 kV leveled off to around 3.6. The difference in temporal profiles between these results and the absorbance (Fig. 4), infers that the pH has little to any significance in changing the color of the solution. Indigo carmine, a common pH indicator, is expected to change from blue to yellow as the pH changes from 11.6 to 14.0.[8] which further supports the idea that the color change is not due to changes in pH. This indicates direct degradation of the dye through plasma-liquid interactions.

B. Gas Flow

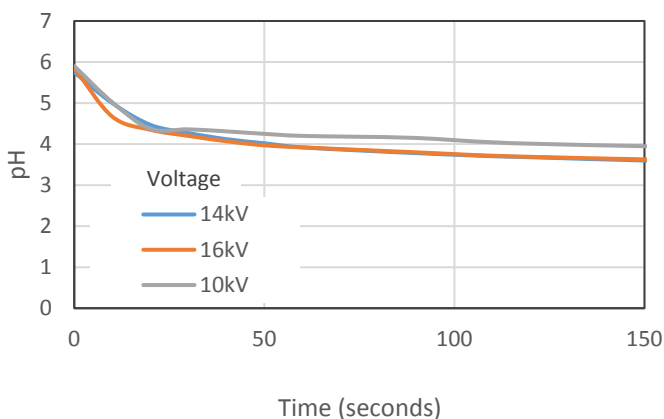Figure 7 displays the effect of gas flow on the pH of the indigo carmine solution at an applied voltage of 14 kV. All three flows after 350 seconds of treatment time decreased to a pH of approximately 4. Flow rates of 10000 SCCM and 5040 SCCM were almost identical, and decreased at a faster rate than a flow rate of 2530 SCCM. After 50 seconds, the higher gas flows produced a pH around 4.5, while 2530 SCCM produced a pH around 5.1.

C. Gas Mixtures

The effect of using a mixture of helium and dry air on the absorption of the 15 mL solution was studied at an applied voltage of 14 kV. The absorption was averaged over wavelengths between 96 and 620 nm. A mixture of 5040 SCCM He and 17 SCCM Air (0.34% air by flow) was compared to 5040 SCCM of pure He. Shown in Fig. 8, the combination of helium and air was more effective than pure helium in lowering the absorbance of indigo carmine. In Fig. 9 the solution's pH change did not show significant differences with the addition of air.

Fig. 6. Effect of applied voltage on pH of 15 mL indigo carmine solution at 4480 SCCM.

To determine how much the concentration of air effects the degradation rate of the indigo carmine, different concentrations of air were added to helium and used to treat a 25 mL solution of indigo carmine solution using an applied voltage of 20 kV. For each mixture, the full spectra was measured every 2 seconds for 10 minutes.

The effect of different air concentrations in helium on the rate of absorbance change for different wavelength is shown in Fig. 10. The absorbance at each wavelength at every 2 second increment was fit to a linear line. The rate of absorbance change was then calculated by obtaining the slope of the linear fit at each wavelength. At approximately 300 nm and 610 nm, significant changes in absorbance was observed, which corresponds to the broken C=C bonds of indigo carmine. Figure 11 displays the rate of absorbance change at 610 nm as a function of air concentration. Surprisingly, the addition of more air decreased the degradation rate of the dye. The magnitude of the rate of absorbance change was greatest at around 9.8×10^{-3} with 100% helium. As more air was introduced, the magnitude of absorption rate decreased at a fairly constant rate when more than 2% air was used. The cause of this sudden jumps in the rate at 1% air is not well understood, however it could be related to changes in plasma density and/or electron kinetics as air is added to He plasma.[9]

IV.   Discussion

The design of this reactor was based upon was creating a large plasma volume along with a large surface area to volume ratio enabling more eff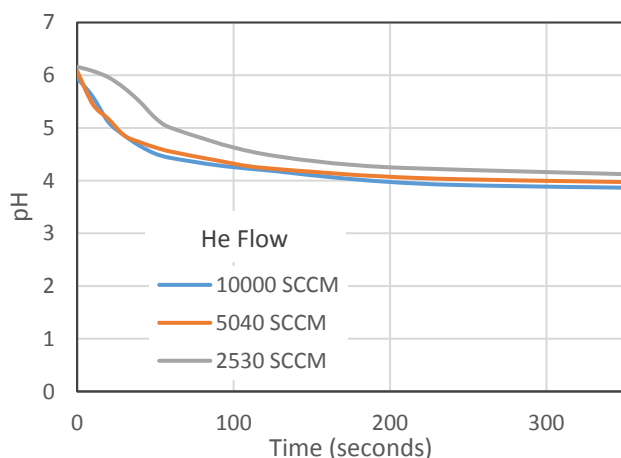ective delivery of reactive species and increasing the rate of dye degradation . This approach is based on studies by Malik,[10] who compared the efficiency of 27 different types of plasma discharge reactors and determined that a thin water film or a spray type of reactor is orders of magnitudes more efficient than a reactor that utilizes a stagnant water source. There is a nearly endless amount of reactor configurations that could be created, however the basic trends of operational parameters still need to be better understood. The foundations of plasma water treatment revolve around the formation of active species that react with volatile organic compounds, with
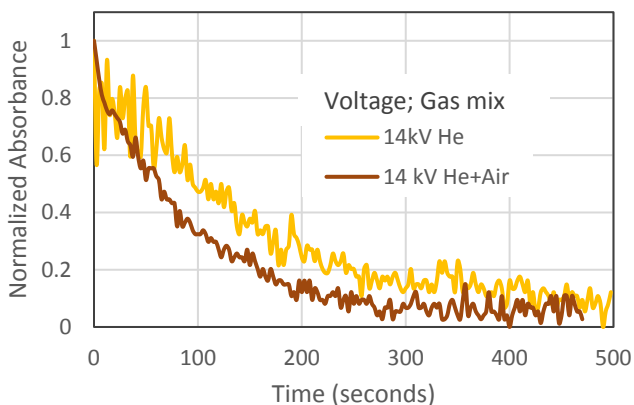

Fig. 7. Effect of He gas flow on pH of 15 mL indigo carmine solution at 14 kV.

Fig. 8. Effect of the addition of air on the absorbance (averaged from 596-620 nm) of indigo carmine solution at 14 kV.

hydroxyl radicals being the main component in dye decomposition. The pertinent chemical reactions in plasma – water interactions were investigated by Jiang,[11] who suggested that water molecules subjected to plasma electrons dissociate and ionize, leading to the production of OH radicals. This can occur directly through dissociation (Eq. 2):

$$H_2O + e \Rightarrow OH^\bullet + H^\bullet + e \quad (2)$$

Or, in step wise processes involving, for example, ionization (Eq. 3) followed by dissociative charge exchange (Eq. 4):

$$H_2O + e \Rightarrow 2e + H_2O^+ \quad (3)$$

$$H_2O^+ + H_2O \Rightarrow H_3O^+ + OH^\bullet \quad (4)$$

With a higher applied voltage, the electric field is stronger, thus increasing the production of plasma species such as OH radicals and potentially increasing dye degradation.

Reactions between OH radicals and an organic compound are characterized by two major processes: abstraction of hydrogen and OH addition to unsaturated organic molecule bonds.[3] Hydrogen abstraction,

$$OH^\bullet + RH \Rightarrow H_2O + R^\bullet \quad (5)$$

can create water and a reactive organic compound, R. The organic radical can react with more OH and O_2 molecules and eventually degrade to CO_2, H_2O, NO_3^-, and other ions through a series of reactions such as,[11]

$$R^\bullet + O_2 \Rightarrow ROO^\bullet \quad (6)$$

$$ROO^\bullet \Rightarrow CO_2 + H_2O + NO_3^- \quad (7)$$
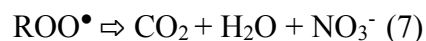
Oxidants also react with indigo carmine, destroying the chromophore double carbon bonds, leading to decolorization. The decomposition of this bond results in a dramatic drop of absorbance at 610 nm.[6]
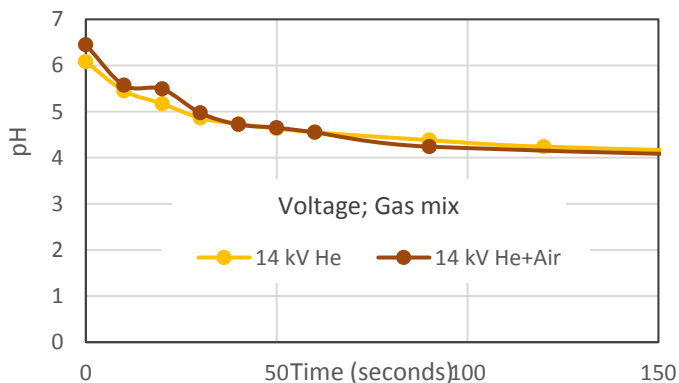

Fig. 9. Effect of the addition of air on the pH of indigo carmine solution at 14 kV.

The production of hydroxyl radicals can also be influenced by the addition of oxygen. Jiang mentions the following chemical reactions involving oxygen in a plasma
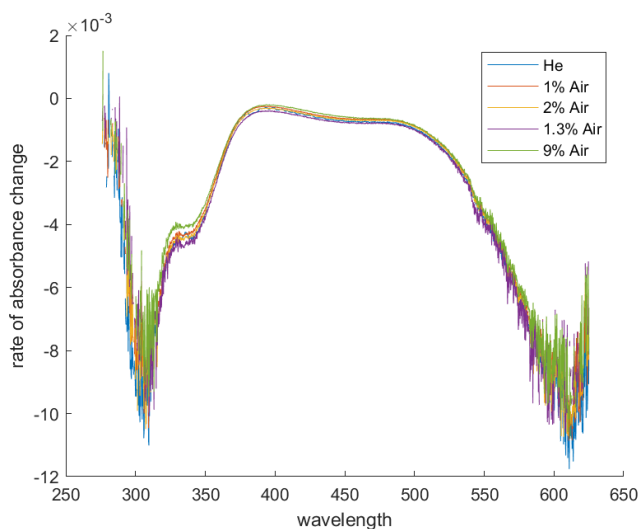
6

Fig. 10. Rate of change of absorbance for the indigo carmine solution when flown through the plasma reactor with difference amounts of air. Each mixture had a total gas flow of 4400 SCCM.
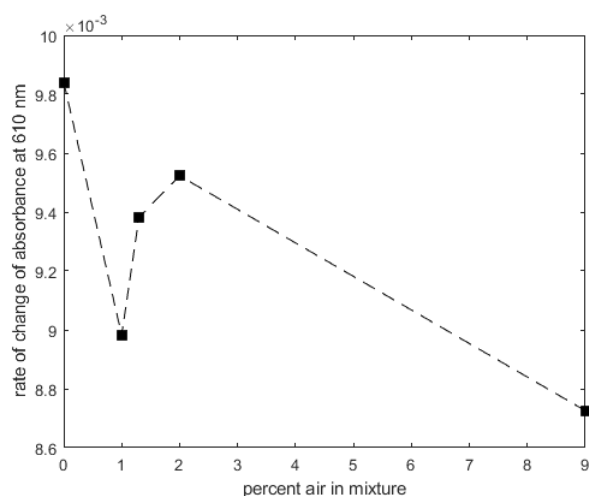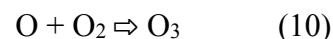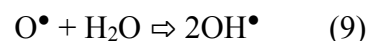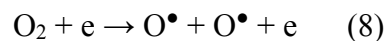

Fig. 11. Rate of absorbance change at 610 nm as a function of percent air in mixture (20 kV applied voltage, 10 min treatment time).

discharge as shown in Eqs. 8-9. Eqs. 10-11 show the reactions for the creation and dissociation of ozone[4] that can lead to the production of OH.

$$O_2 + e \rightarrow O^\bullet + O^\bullet + e \quad (8)$$

$$O^\bullet + H_2O \Rightarrow 2OH^\bullet \quad (9)$$

$$O + O_2 \Rightarrow O_3 \quad (10)$$

$$3O_3 + H_2O \Rightarrow 2OH^\bullet + 3O_2 \quad (11)$$

Introducing a very small amount of air into the gas mixture in this work may have produced more hydroxyl radicals due to a greater concentration of oxygen. Ultimately, this could lead to more organic compound breakdown due to radicals. However, the relationship between the amount air and absorbance did not follow a simple positive correlation. A study by Wang *et al.* determined the optimal gas mixture of helium and oxygen for the decolorization of methyl violet.[12] It is important to note that methyl violet has a very similar molecular structure to indigo carmine; both chemicals have a reactive C=C bond that result in decolorization when broken. A 3:1 ratio of helium to oxygen was determined to be the most efficient, as higher and lower ratios of oxygen were less efficient. Spectrums of helium and helium-oxygen discharges showed that more atomic oxygen was emitted in a helium-oxygen discharge. However, the reactor configuration and power supply in their work differed significantly from the configuration here. The study concluded that utilizing helium provided a more energy efficient discharge, while the addition of oxygen greatly promoted the production of oxidants.

In the present study, the addition of 17 SCCM air – or 0.34% air by flow - achieved a more effective dye degradation compared to only helium. However, the addition of 1%, 1.3%, 2%, and 9% air was less effective. However, the additions of >1% air could possibly have led to more energy consumption due to the vibrations of molecules like nitrogen, rather than more dissociation
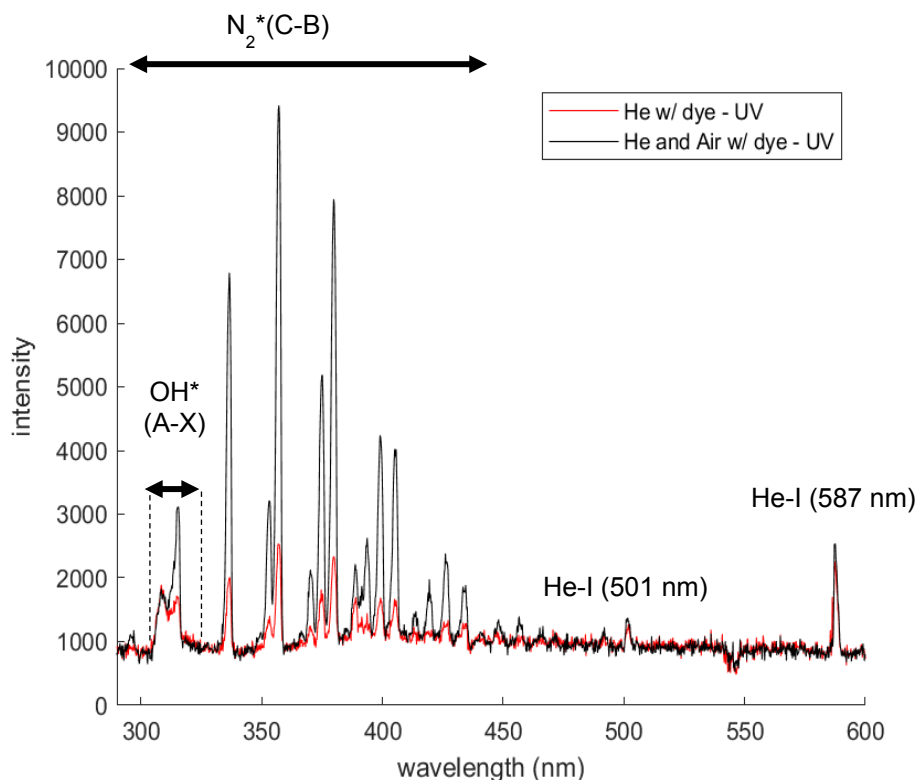
Fig. 11. Emission spectrum of discharges in He (4400 SCCM) and
He+Air (He: 4000 SCCM, Air: 268 SCCM) at 18 kV.

of water and/or the production of reactive oxygen species. Fig. 11 compares OES measurements on a plasma discharge with 6.3% air to a discharge with pure helium at 18 kV. Both spectra contained emission lines from $OH^\bullet$, N_2, and He. The intensity of $OH^\bullet$ and He in both discharges were similar, however the major difference was in the amount of N_2 in the discharge with air. In order to test if excess amounts of nitrogen inhibits the dissociation of water molecules and production of $OH^\bullet$, an OES measurement of a discharge with only oxygen added to the gas mixture would be beneficial. Also, OES measurements in the 700-800 nm range would be helpful in comparing the intensity of oxygen, which plays a crucial role in forming oxidizing species. Similarly to Wang's study,[12] it is likely that more atomic oxygen will be produced when air is added. Further study between 0% and 1% of air is necessary to determine the optimal gas mixture.

The formation of acids from plasma treatment dramatically lowered the pH of the treated solution. When air was used as the background gas, the formation of nitric acid was observed in other studies due to the presence of nitrogen and oxygen.[4] However, in Fig. 7, the pH change when using just helium or a mixture of helium/air was almost identical, thus inferring that nitric acid is not the only species responsible for lowering the pH. Shainksy *et al.* investigated the formations of acid in a plasma discharge formed in oxygen. It was determined that organic acids formed due to the reactions between hydrogen (H^+) and superoxide (O_2^-) ions without the presence of nitrogen.[13] It is reasonable to assume such species or air could be introduced using the system described here even when only helium gas is used. Indeed, hydrogen and superoxide could be derived from water vapor in a helium plasmas and recirculating the solution could carry dissolved air into the plasma zone.

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V. Conclusion

Applied voltage and gas mixtures were investigated for the optimization of indigo carmine treatment. Each operating parameter involved increasing the amount of oxidants, especially the hydroxyl radial, thus directly affecting the degradation rate. The highest tested voltage of 18 kV produced the fastest absorbance change. Although the effect of gas flow on absorbance was not measured, it is predicted that higher gas flows would result in a faster absorbance decrease due to the increase in oxidants and/or a decrease in the size of the water droplets. The addition of 0.34% air into the gas mixture proved to be beneficial as it increased degradation rates, but the addition of more than 1% air decreased the degradation rate. Further studies are needed to determine the optimal concentration of air which produces the most efficient degradation of indigo carmine.

The chemical and physical analysis of plasma-based water treatment is still not well understood.[5] Utilization of technologies such as Raman spectroscopy can allow for a more complete understanding on the products created. As the optimization of operating parameters is making energy consumption more efficient, the application of plasma wastewater treatment looks promising.

VI. Acknowledgements

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